

neighbors H<sub>2</sub>O molecules is 7.2; this quantity increases with  $d_2$  leading to the numbers reported in Figure 6 and in simulation studies for simple gaseous solutes.

The dissolution of nonpolar gases in water is successfully reproduced by the hard-sphere perturbation treatments for the simple reason that dissolution entails the creation of a cavity which starts growing from a natural void in the liquid. Viewed from the positions occupied by the nonpolar solutes, water does not differ too much from a hard-sphere fluid having the same molecular size and number density. Furthermore, the temperature dependence of the dissolution properties is correctly given if the experimental change of density with temperature for the pure solvent is employed.

In other words, the dissolution of small nonpolar solutes in water does not involve significant reorientation of the neighboring water molecules. If this were the case, a hard-sphere perturbation theory would not be capable of describing the thermodynamics of the process over a wide temperature range. This is in agreement with the view expressed above that the large negative  $\Delta S^\circ_2$  is not the origin of the low solubility in aqueous medium, but rather the consequence. The orientation of H<sub>2</sub>O molecules surrounding an empty point or a nonpolar solute in liquid water is obviously

very different from that of the solvent molecules surrounding a lattice point where a central H<sub>2</sub>O molecule is sited. It seems that in many instances reorientation of water molecules has been invoked because this point has been overlooked.

In order to verify our description of the dissolution of nonpolar solutes in water, the following points could be studied either by simulation or experiment: (1) the average orientation of the first H<sub>2</sub>O neighbors to empty points in the pure liquid, compared to the distribution of first neighbor water molecules surrounding spherical nonpolar solutes of variable size (including  $d_2 = 0$ ); (2) accurate determination of the thermodynamics of transfer of an inert gas from D<sub>2</sub>O to H<sub>2</sub>O over a wide temperature range; (3) the average total electric field on a nonpolar spherical molecule.

**Note Added in Proof.** Recently Wood and co-workers (*J. Phys. Chem.*, in press) have determined experimentally  $C_p^\circ_2$  for Ar in H<sub>2</sub>O up to 578 K. These important experimental data can be successfully reproduced by the perturbation treatment presented here by using the same molecular parameters (work to be submitted for publication). This is strong evidence in favor of the views expressed in this article.

## The Single Electron Shift as a Fundamental Process in Organic Chemistry: The Relationship between Polar and Electron-Transfer Pathways

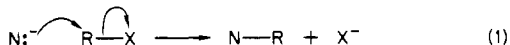
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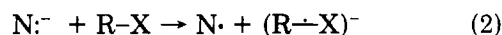
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The concept of electronic reorganization is a fundamental tenet of chemistry. Chemical reactions come about through the rearrangement of valence electrons. It is these electrons that hold the atoms together in the reacting molecules and which, by redistribution, govern the structure of the product molecules.

Yet a strange dichotomy concerning the movement of electrons during chemical reactions has emerged over the years. In electron-transfer theory a fundamental postulate is that electrons may only be transferred one at a time.<sup>1,2</sup> But, within organic chemistry, for polar reactions at least, electrons are considered to move about in pairs, as illustrated by the S<sub>N</sub>2 process (eq 1).



It is only for radical producing reactions that the idea of a single electron transfer (SET) is widely entertained, as illustrated by the first step of the S<sub>RN</sub>1 pathway for nucleophilic substitution (eq 2).<sup>3</sup> This subdivision of



nucleophilic substitution reactions into either polar or SET pathways is equally applicable to all the other fundamental organic mechanisms. Thus hydride reduction, electrophilic, and nucleophilic aromatic substitution, and nucleophilic addition, to quote a few examples, may also be formulated in terms of either SET or polar mechanisms.

Recognition of the SET pathway in organic reactions has grown enormously over the last 20 years, primarily following the pioneering work of Kornblum, Russell, and Bunnett.<sup>3-7</sup> The impact of SET pathways on organometallic chemistry has been extensive, largely due to the contributions of Kochi and co-workers.<sup>8,9</sup> More

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(1) Semenov, N. N. "Some Problems in Chemical Kinetics and Reactivity"; Princeton University Press: Princeton, 1958.

(2) For a recent excellent review on organic electron transfer reactions, see: Ebersson, L. *Adv. Phys. Org. Chem.* 1982, 18, 79.

(3) Bunnett, J. F. *Acc. Chem. Res.* 1978, 11, 413.

(4) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 734.

(5) Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* 1966, 88, 5663; 1968, 90, 347.

(6) Kim, J. K.; Bunnett, J. F. *J. Am. Chem. Soc.* 1970, 92, 7463, 7464.

(7) Application of electron transfer concepts in organic chemistry by Soviet workers has been popular for many years. For reviews, see: (a) Todres, Z. V. *Russ. Chem. Rev. (Engl. Transl.)* 1978, 47, 148; (b) Bilevich, K. A.; Okhlobystin, O. Y. *Russ. Chem. Rev. (Engl. Transl.)* 1968, 37, 1.

recently Ashby and co-workers<sup>10</sup> have greatly extended the list of organic reactions thought to proceed via SET. Many classic organic reactions, long thought to operate via a polar pathway, now appear to proceed via radical intermediates.<sup>10,11</sup>

Yet, despite the growing evidence that SET processes are far more widespread than originally thought, the relationship between SET and polar pathways remains obscure. Why do electrons at times appear to move in pairs but at other times to transfer one at a time?<sup>12</sup> The formalism of one-electron and two-electron pathways on its own is of little value in gauging under what circumstances one pathway is likely to be preferred over the other. The only definite point concerning the polar-SET dichotomy is the operational distinction, which focuses on the ability to detect free radical intermediates during the course of the reaction.

In view of the existing uncertainty concerning this dichotomy, a number of questions arise: (i) What are the factors that determine whether a particular reaction proceeds via SET or a polar pathway? (ii) What is the precise relationship between the two possible processes? (iii) Do the SET and polar pathways represent discrete routes or is there a mechanistic spectrum bridging between these two mechanistic extremes? In seeking to provide answers to the above questions, the present Account sets out to demonstrate that all so-called two-electron (or polar) pathways actually involve the shift of a single electron and are far more closely related to the established SET pathways than has been recognized till now. While this view has been expressed by others,<sup>14,15</sup> it seems fair to say that the chemical community remains, as yet, unconvinced. We now present theoretical, spectroscopic, electrochemical, and chemical evidence that many conventional organic reaction mechanisms are best understood in terms of a single electron shift process.<sup>16</sup>

(8) For a comprehensive monograph of early work, see: Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

(9) For more recent work, see: (a) Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* 1981, 103, 5839. (b) Fukuzumi, S.; Kochi, J. K. *Ibid.* 1980, 102, 2141, 7920. (c) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *Ibid.* 1980, 102, 2928. (d) Wong, C. L.; Kochi, J. K. *Ibid.* 1979, 101, 5593. (e) Fukuzumi, S.; Mochida, K.; Kochi, J. K. *Ibid.* 1979, 101, 5961. (f) Mochida, K.; Kochi, J. K.; Chen, K. S.; Wan, J. K. S. *Ibid.* 1978, 100, 2927.

(10) (a) Ashby, E. C.; Goel, A. B. *J. Am. Chem. Soc.* 1981, 103, 4983. (b) Ashby, E. C.; Bowers, J. R. *Ibid.* 1981, 103, 2242. (c) Ashby, E. C.; Goel, A. B.; DePriest, D. N.; Prasad, H. S. *Ibid.* 1981, 103, 973. (d) Ashby, E. C.; Goel, A. B.; DePriest, R. N. *Ibid.* 1980, 102, 7779. (e) Ashby, E. C.; Wiesman, T. L. *Ibid.* 1978, 100, 189. (f) Ashby, E. C.; Argyropoulos, J. N.; Meyer, G. R.; Goel, A. B. *Ibid.* 1982, 104, 6788. (g) Ashby, E. C.; Goel, A. B.; DePriest, R. N. *J. Org. Chem.* 1981, 46, 2429.

(11) Chung, S.-K. *J. Chem. Soc. Chem. Commun.* 1982, 480.

(12) Ebersson has proposed that the reaction of nucleophiles toward radical cations as either reductants or as nucleophiles may be understood on the basis of the Dewar-Zimmerman rules,<sup>13</sup> see: (a) Ebersson, L. *Tetrahedron* 1978, 34, 731; (b) *J. Chem. Soc., Chem. Commun.* 1975, 826. For contradictory views, see: (c) Evans, T. R.; Hurysz, L. F. *Tetrahedron Lett.* 1977, 3103. (d) Rozhkov, I. N.; Gambaryan, R. P.; Galpern, E. G. *Tetrahedron Lett.* 1976, 4819.

(13) (a) Dewar, M. J. S. *Angew. Chem., Int. Ed. Engl.* 1971, 10, 761.

(b) Zimmerman, H. E. *Acc. Chem. Res.* 1971, 4, 272.

(14) Bank, S.; Noyd, D. A. *J. Am. Chem. Soc.* 1973, 95, 8203.

(15) (a) Flesia, E. unpublished, quoted in ref 15b. (b) Chanon, M.; Tobe, M. L. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 1.

(16) In this paper we distinguish between the terms "electron transfer" and "electron shift". *Electron transfer* refers to a simple redox process in which the overall change that has occurred is the transfer of a single electron. This is in agreement with current usage. A change in the position of an electron which is, in addition, coupled to bonding changes is termed an *electron shift*. Thus polar reactions which involve a DA - D<sup>+</sup>A<sup>-</sup> avoided crossing are termed electron shift. Electron shift processes do not necessarily result in free radical formation.

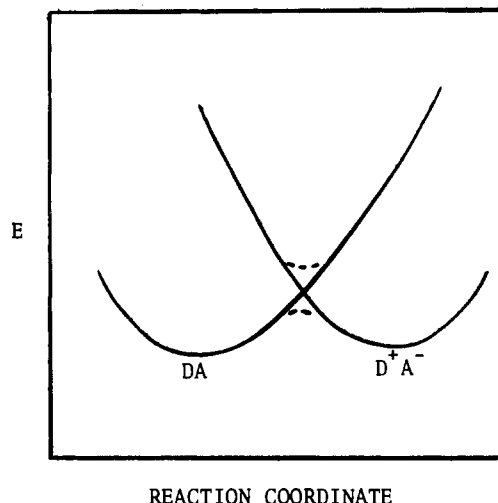
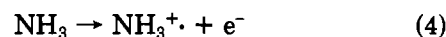
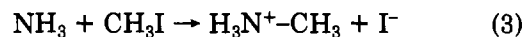


Figure 1. Schematic energy diagram illustrating an electron-transfer reaction based on the intersection of two configuration curves, DA and D<sup>+</sup>A<sup>-</sup>.

### Theoretical Considerations

In electronic terms, there is a fundamental similarity between polar and SET processes. Consider the S<sub>N</sub>2 reaction of NH<sub>3</sub> and CH<sub>3</sub>I (eq 3) and the act of ionization of NH<sub>3</sub> (eq 4). Both processes result in the N



atom formally acquiring a single positive charge. This must mean that in both processes the N atom has lost a *single* electron, which, in the case of eq 3, ends up on I<sup>-</sup>. While this might appear obvious, we state it nonetheless, since there appears to be a widespread belief that somehow the number of electrons involved in the above two processes is different—that *two* electrons are involved in eq 3 while only one is involved in eq 4. This is simply not the case and confuses the real differences that do exist between SET and polar pathways.

In order to appreciate more fully the physical distinction between SET and polar reactions, let us build up the reaction profile for each pathway using the configuration mixing (CM) model.<sup>17,18</sup> The essence of the CM model is that a simple description of any reaction profile may be obtained from a schematic energy plot of key electronic configurations that describe reactants, products, and potential intermediates.<sup>17</sup>

**Reaction Profile for a SET Pathway.** A schematic reaction profile for electron transfer between an electron donor (D) and an acceptor (A) appears in Figure 1. The two curves are plots of the energies of the electron configurations for the donor-acceptor pair before electron transfer (the DA curve) and after electron transfer (the D<sup>+</sup>A<sup>-</sup> curve). The reaction pathway con-

(17) (a) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* 1982, 104, 187. (b) Shaik, S. S.; Pross, A. *Ibid.* 1982, 104, 2708. (c) Pross, A.; Shaik, S. S. *Tetrahedron Lett.* 1982, 5467. (d) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* 1983, 16, 363. (e) Pross, A. *Adv. Phys. Org. Chem.*, in press. (f) McLennan, D. J.; Pross, A. *J. Chem. Soc., Perkin Trans. 2* 1984, 981.

(18) For earlier work on the CM model see: (a) Epiotis, N. D.; Shaik, S.; Zander, W. In "Rearrangements in Ground and Excited States"; Mayo, P., Ed.; Academic Press: New York, 1980. (b) Epiotis, N. D.; Shaik, S. In "Progress in Theoretical Organic Chemistry"; Csizmadia, I. G., Ed.; Elsevier: Amsterdam, 1977; Vol. 2. (c) Epiotis, N. D. "Theory of Organic Reactions"; Springer-Verlag: Heidelberg, 1978. (d) Fukui, K. "Theory of Orientation and Stereoselection"; Springer-Verlag: Heidelberg, 1975. (e) Shaik, S. S. *J. Am. Chem. Soc.* 1981, 103, 3692.

sists of solvation changes and geometric distortions which raise the energy of the DA complex till it becomes about isoenergetic with  $D^+A^-$ . At this point the electron is transferred and the complex relaxes to give  $D^+$  and  $A^-$ . It is apparent that the CM treatment for electron transfer merges smoothly with Marcus theory,<sup>19</sup> so no further detail is required.

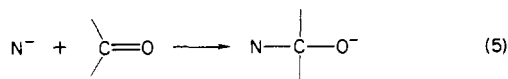
**Reaction Profile for a Polar Pathway.** Let us now consider the preeminent polar process, the  $S_N2$  reaction. In a number of recent papers we have analyzed the  $S_N2$  reaction in terms of both MO and VB configurations.<sup>17b-f</sup> These papers have demonstrated that the electronic relationship between reactants and products in an  $S_N2$  reaction is a *single electron shift*<sup>16</sup> and therefore may also be described by a  $DA-D^+A^-$  avoided crossing. In order to convert the wave function describing reactants to one describing products, one need only shift a single electron from D to A. This may also be demonstrated with the aid of valence bond (VB) configurations; configuration 1 is the predominant VB contributor to the reactants while 2 is the corresponding major contributor to products. Conversion of 1 to 2 requires nothing more than a single electron shift from  $N^-$  to X.<sup>17c,d</sup>



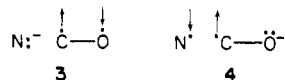
If both electron-transfer and  $S_N2$  pathways are described by a  $DA - D^+A^-$  crossing, then the following questions immediately arise: What is the distinction between these two processes? Why are radicals generated in the former case but not in the latter case? In order to answer these questions, we must first probe the consequence on bonding within the DA complex of an electron transfer from the D to the A moiety.

For a SET process the answer to this last point is simply: there is no substantive change in bonding as a result of the electron transfer. D and A react to simply yield  $D^+$  and  $A^-$ . For polar processes however the actual electron shift leads to structural reorganization within the reaction complex so that the reaction product of D and A is *something other than  $D^+$  and  $A^-$* . Two general pathways are feasible: (a)  $D^+$  and  $A^-$  combine to form one molecule by *group coupling* and (b) a radical fragment contained with the  $A^-$  moiety is cleaved off and combines with  $D^+$  in what constitutes a *group transfer*. Let us consider these possibilities in more detail.

**Group Coupling.** The process of group coupling, as a result of the electron shift, may be illustrated by the reaction of nucleophilic addition to a carbonyl group (eq 5). For this reaction, VB representations of reac-

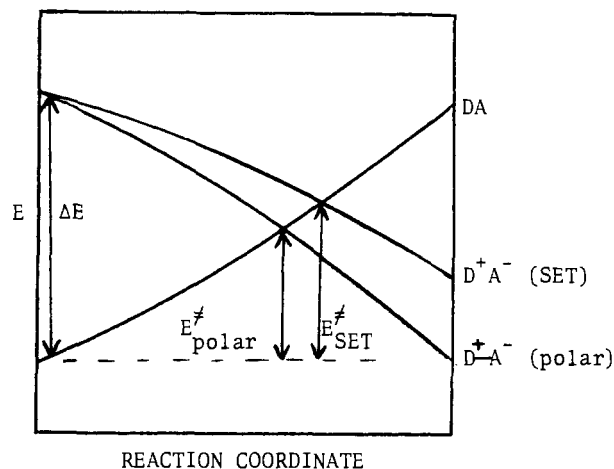


tant and product configurations are 3 and 4, respectively. The key point here is that as a consequence of



(19) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A. In "Special Topics in Electrochemistry"; Rock, P. A., Ed.; Elsevier Amsterdam, 1977.

(20) Pauling, L.; Wilson, E. B., Jr. "Introduction to Quantum Mechanics"; McGraw-Hill: New York, 1935.



**Figure 2.** Schematic energy diagram illustrating the  $DA - D^+A^-$  crossing for competing SET and polar pathways.  $E^*$  for the polar process is less than for the SET process. (Strictly speaking, the two  $D^+A^-$  curves should be presented in separate diagrams since the reaction coordinates for polar and SET processes are different. For convenience of comparison the two appear on the one diagram.)

the electron shift from  $n_N \rightarrow \pi^*_{CO}$  to form  $D^+A^-$ , two spin-paired electrons in close proximity to each other, on N and C, are generated. Coupling of these two electrons into a single bond leads to the formation of the nucleophilic addition products. Thus the overall result of the electron shift is to generate a  $D^+A^-$  molecular entity and not  $D^+$  and  $A^-$  species as in the SET pathway.

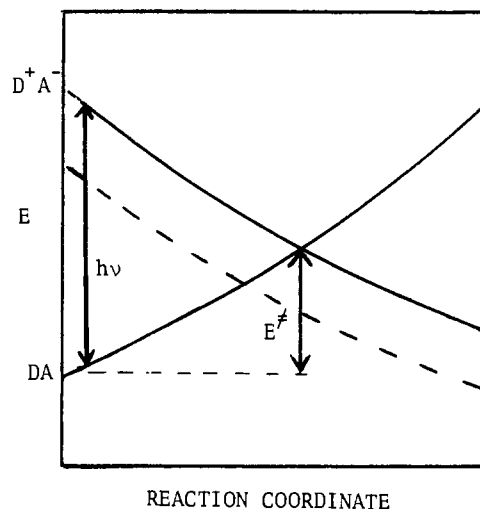
**Group Transfer.** The process of group transfer occurring synchronously with an electron shift is exemplified by the  $S_N2$  reaction (eq 1). An electron shift from the nucleophile N into the  $\sigma^*_{R-X}$  orbital substantially weakens the R-X linkage. In fact, since the primary VB contributor to the  $(R-X)^-$  moiety is  $R:X^-$ , which is repulsive between R and X groups, the stage has been set (configurationally speaking) for a group transfer. *An electron shift from N to RX has resulted in the breaking of the R-X linkage as well as to bring the two radical groups N· and R· in close proximity.* The result is group transfer. Of course, no free radical intermediates need actually be formed in the group coupling or the group-transfer routes. In both cases one spin-coupled electron pair (e.g., 3) is converted to some other spin-coupled pair (e.g., 4).<sup>17d</sup>

Let us summarize the present discussion by the diagram of Figure 2. Both so-called polar and SET processes come about through the crossing of  $DA$  and  $D^+A^-$  configuration curves, i.e., through a single electron shift. The polar pathway however is commonly favored since stabilizing bonding changes occur synchronously with and as a direct consequence of the electron shift. These stabilizing bonding changes lead to the  $D^+A^-$  curve for the polar reaction falling *more steeply* than the corresponding curve for the electron transfer reaction. As a result, a lower energy of activation for the polar process,  $E^*_{polar}$ , compared to that for the SET pathway,  $E^*_{SET}$ , is obtained (avoided crossings have been deleted for clarity). Factors that are likely to reverse this preference are discussed subsequently. Let us now analyze experimental data (electrochemical, chemical, and spectroscopic) that lend support to the model described and demonstrate its usefulness.

## Experimental Considerations

**Electrochemical Evidence.** If the preceding theoretical analysis has any factual basis whatever, then it is evident that a comparison of chemical and electrochemical processes should clearly show up the common denominator, the single electron shift. After all, it is within the realm of electrochemistry that the role of single electron transfer is unchallenged. On the basis of the previous discussion we noted that a single electron shift may lead to either a SET pathway, or, alternatively, to a polar pathway if the electron shift is accompanied by certain bonding changes (group coupling or group transfer). Precisely the same general picture emerges in electrochemical studies.<sup>2</sup> For example, electrochemical reduction of a methyl halide involves more than just electron transfer to yield a methyl halide radical anion.<sup>21</sup> As we noted above, the methyl halide radical anion lies on a dissociative surface and is therefore unstable with respect to cleavage of the C-X bond. Thus electrochemical reduction cleaves the methyl halide into a methyl radical and a halide ion. The analogy with the chemical pathway, the S<sub>N</sub>2 reaction, is apparent. Here, also, the methyl halide is cleaved by an electron shift. The only difference between these two processes is that in the S<sub>N</sub>2 reaction the nucleophile radical species is present and is coupled to the incipient methyl radical. As a result the products of the chemical reaction are N-CH<sub>3</sub> and X<sup>-</sup> rather than CH<sub>3</sub>· and X<sup>-</sup>, obtained electrochemically.

The analogy between chemical and electrochemical electron-transfer processes may be extended. We can confirm our earlier supposition that, in general, during a chemical electron shift the polar pathway is preferred over the SET route. For any given electrochemical process the intrinsic electrochemical potential (ignoring specific kinetic effects) is smaller in value for the irreversible electron transfer, where some bonding changes are occurring in addition to the electron transfer, than the standard potential,  $E^\circ$ , for the reversible redox couple.<sup>2</sup> This is because, by undergoing some bonding changes synchronously with the electron transfer, the intrinsic electrode potential required to bring about that electron transfer is reduced. The irreversible pathway, if available, is thermodynamically favored over the reversible one.<sup>22</sup> The same pattern seems to hold for chemical electron transfer. Indeed, for the case of a chemical electron transfer, it is quite likely that without the coupled chemical reaction, electron transfer is endergonic and cannot take place.<sup>26</sup> Thus on the basis



**Figure 3.** Schematic energy diagram showing the effect of stabilization of the  $D^+A^-$  configuration curve (dotted line) on both the energy of the charge-transfer band,  $h\nu$ , for the DA complex and the activation barrier,  $E^\ddagger$ ; both  $h\nu$  and  $E^\ddagger$  are reduced.

of the electrochemical analogy, polar pathways are expected in general to be energetically more favored than competing SET pathways.

**Spectroscopic Evidence.** In addition to the electrochemical evidence discussed above there exists spectroscopic support for the notion that the reaction profile for many polar processes may be viewed as an avoided crossing of DA and  $D^+A^-$  configurations. Kochi and co-workers have observed in a number of polar reactions such as electrophilic aromatic substitution in arenes<sup>27a,c</sup> and electrophilic addition to alkenes by molecular bromine<sup>27b,c</sup> that  $\log k$  for reaction is linearly related to the charge-transfer transition energies,  $h\nu$ , of the reacting molecules. This point is highly significant since in some way *the barrier for the polar reaction is related to the energetics of transferring a single electron from one reactant to the other (DA to  $D^+A^-$  excitation)*. Inspection of Figure 3 reveals the basis for the correlation of barrier height and charge-transfer bands. If the barrier height is governed by the DA- $D^+A^-$  crossing, then it is apparent why the DA to  $D^+A^-$  excitation ( $h\nu$ ) correlates with the reaction barrier. Introducing a better donor molecule, D, lowers the entire  $D^+A^-$  curve (indicated by the broken line) so that both the charge-transfer band frequency,  $h\nu$ , as well as the barrier height,  $E^\ddagger$ , are decreased. This is just a simple application of the Bell-Evans-Polanyi<sup>28</sup> diagram in which the anchor point for the excited configuration is given a physical meaning: the excited charge-transfer state  $D^+A^-$  of the reactants. Thus a DA- $D^+A^-$  crossing for polar processes is consistent with Kochi's experimental observations. Furthermore, the fact that Kochi has observed similar correlations in a wide range of organic and organometallic reactions<sup>8,9,27</sup> strongly supports the idea that reactions governed by a DA- $D^+A^-$

(21) (a) Casonova, J.; Ebersson, L. In "The Chemistry of the Carbon-Halogen Bond" Patai, S., Ed.; Wiley: London, 1973; p 979. (b) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Non-Aqueous Systems"; Marcel Dekker: New York, 1970.

(22) For example, the  $E_p$  value for the electrochemical oxidation of benzene under conditions favoring a reversible process is 3.03 V<sup>23a</sup> (vs. NHE), while under less favorable conditions an  $E_p$  value of 2.6 V<sup>23b</sup> was measured. A similar effect has been noted by Miller,<sup>24</sup> who found that the NADH/NADH<sup>+</sup> redox couple becomes more positive in the absence of a coupled proton transfer from the NADH<sup>+</sup> product (to yield NAD<sup>+</sup>). In fact as Ebersson has demonstrated the more reactive the electrochemical product, the larger the difference between  $E^\circ$  and  $E_p$  values.<sup>2,26</sup> This difference between  $E^\circ$  and  $E_p$  is attributed to the stabilizing influence of some coupled chemical reaction.

(23) (a) Jensen, B. S.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 5211.

(b) Osa, T.; Yildiz, A.; Kuwana, T. *J. Am. Chem. Soc.* **1969**, *91*, 3994.

(24) Carlson, B. W.; Miller, L. L. *J. Am. Chem. Soc.* **1983**, *105*, 7453.

(25) Ebersson, L.; Wistrand, L. G. *Acta Chem. Scand., Ser. B* **1980**, *B34*, 349.

(26) A case in point that has been characterized in detail by Schuster and co-workers concerns the chemically initiated electron-exchange luminescence of dimethyldioxetane. See: (a) Schmidt, S. P.; Schuster, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 1966. (b) Schuster, G. B.; Schmidt, S. P. *Adv. Phys. Org. Chem.* **1982**, *18*, 187.

(27) (a) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 7240. (b) Fukuzumi, S.; Kochi, J. K. *Ibid.* **1980**, *103*, 2783. (c) Fukuzumi, S.; Kochi, J. K. *Ibid.* **1982**, *104*, 7599. (d) Fukuzumi, S.; Kochi, J. K. *Tetrahedron* **1982**, *38*, 1035.

(28) (a) Bell, R. P. *Proc. R. Soc. London, Ser. A* **1936**, *154*, 414. (b) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11.

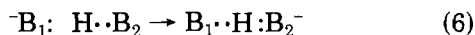
crossing are extremely general.

**Factors Governing SET vs. Polar Pathways.** The DA-D<sup>+</sup>A<sup>-</sup> avoided crossing model for both polar and electron-transfer reactions has immediate reactivity consequences. It implies that the transition state for both processes is likely to be similar, particularly when the preference for one pathway over the other is slight.<sup>29</sup> It also suggests that we have the means to specify those factors that will tend to encourage one pathway over the other. The key point that forms the basis for the entire analysis that follows is: *since both SET and polar pathways involve a single electron shift in the transition-state region, the factor that determines which particular pathway is followed in any given reaction is the feasibility of coupling of the two spin-paired electrons following the electron shift. Any factor (steric, electronic or geometric) that operates so as to inhibit or hinder the coupling process will tend to favor a SET pathway over a polar one.* Let us now discuss the various factors in detail.

**Effect of Electronic Structure of Donor and Acceptor.** The reaction of organic molecules with the alkali metals has long been discussed in terms of a SET process. The only distinction between an alkali metal and any two-electron nucleophile is that the absence of an odd electron on the metal *after* electron transfer eliminates the possibility of a polar process. Having given up its only valence electron, the metal is incapable of interacting chemically with the A<sup>-</sup> moiety; a SET process results. Of course, electrochemical reduction falls into the same category. Thus the difference between a one-electron donor (e.g., Na) and a so-called two-electron donor (e.g., HO<sup>-</sup>) lies not in the *number* of electrons transferred but in the ability of the oxidized form of the two-electron donor (i.e., HO<sup>•</sup>) to undergo a bonding interaction with the reduced substrate A<sup>-</sup>.

While the case of a SET process for alkali metals might be considered an obvious one, the unusually slow rate of protonation of certain radical anions provides a more subtle example of the same fundamental type.<sup>30</sup> Indeed Ebersson<sup>12a</sup> has estimated that radical anions protonate 10<sup>4</sup>–10<sup>7</sup> times more slowly than carbanions of similar structure. What is the reason for the low kinetic basicity of radical anions?

Viewing the proton transfer reaction as an *electron shift* (B<sub>1</sub> to B<sub>2</sub>) followed by a hydrogen atom shift (B<sub>2</sub> to B<sub>1</sub>), eq 6, provides new insight into the problem.<sup>31</sup>



The act of transferring a single electron from a radical anion, such as diphenylacetylene radical anion, does *not* leave behind an odd electron (on B<sub>1</sub>) capable of bonding to the hydrogen atom. This is because *no single electron remains after electron transfer*; the stable neutral molecule has been regenerated. Thus the radical anion will tend to react as a *reductant* rather than as a *base*, because in this way the stable electronic configuration obtained *after* electron transfer does not need to be disturbed.<sup>31</sup>

**Effect of Donor–Acceptor Ability.** A prime factor in governing the relative importance of the polar and

SET routes is the donor and acceptor ability, or taken together, IP<sub>D</sub>–EA<sub>A</sub>, for the DA pair. The better the donor–acceptor pair, the earlier the avoided crossing as can be seen in Figure 3. This means that the electron shift takes place *early* along the reaction coordinate where the energetic impact of bond making does not significantly manifest itself. *Thus the better the donor–acceptor pair, the more likely it becomes that little or no covalent bond formation has taken place in the transition state, thereby facilitating the SET route and subsequent formation of free radicals.* This pattern has indeed been observed by Kochi<sup>32</sup> for the reaction of a series of alkyl radicals with transition-metal complexes of phenanthroline, by House<sup>33</sup> for the addition reaction of organocuprates to carbonyl compounds, and by Evans and Blount<sup>34</sup> for reaction of diphenylanthracene cation radical with nucleophiles. Also, Arnett,<sup>35</sup> Russell,<sup>36</sup> and Zieger<sup>37</sup> have noted that less stable carbanions tend to react with carbocations and benzyl halides via a SET pathway, while more stable carbanions prefer the polar route, as expected from the model. The SET mechanism proposed by Perrin<sup>38</sup> for aromatic nitration is also consistent with this view. Furthermore, Ritchie's<sup>39</sup> observation that nucleophilic reactivity toward a reactive substrate correlates with nucleophile solution ionization potential and Hoz's discussion<sup>40</sup> of partial electron transfer to explain the α-effect and cation–anion combination reactions are also both consistent with the idea that reactivity in good D–A systems are largely governed by the energetics of the single electron shift.

**Effect of Steric Interactions between D and A.** From the earliest studies involving the SET pathway it became apparent that sterically hindered molecules show a greater preference for the SET route than similar uncrowded molecules. For example, Ashby has found that the reaction of dimesityl ketone with Grignard reagents<sup>10a</sup> and lithium diisopropylamide with alkyl halides<sup>10g</sup> proceed via SET pathways rather than the polar pathway that is followed by less crowded analogues. The competition between polar and SET routes for reaction of alkyl radicals and metal complexes has also been demonstrated by Kochi to be sensitive to steric effects.<sup>32</sup> Steric hindrance invariably favors SET over the polar pathway.

Inspection of Figure 2 suggests why steric hindrance favors the SET route. As noted previously, the D<sup>+</sup>A<sup>-</sup> configuration is expected to come down in energy more steeply along the *polar* reaction coordinate than the SET reaction coordinate. This is because the polar process leads to energetically favorable bonding changes (group coupling or group transfer). However for these bonding changes to manifest themselves energetically, the reacting species must approach each other to within bonding distances (less than 2 Å). If steric hindrance

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(29) Walling has recently reached a similar conclusion. See: Walling, C. *J. Am. Chem. Soc.* **1980**, *102*, 6854.

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is significant, then the energy lowering due to the bonding changes will be partially canceled by the steric repulsions generated in the transition state. If the steric factors are particularly large, this may lead to a reversal in barrier height with the lower barrier actually found in the SET process. Since electron transfer in SET processes may take place at distances significantly greater than those at which incipient bonding takes place,<sup>41</sup> the sensitivity of the  $D^+A^-$  curve for the SET pathway to the same steric factors is expected to be smaller in comparison. Thus we see that steric hindrance is expected to favor the SET pathway over the polar one.

**Effect of the D-A Bond Strength.** As we have already noted, the major difference between polar and SET pathways focuses on the bond formed between  $D^+$  and  $A^-$  in the polar process. It is evident therefore that the *strength* of the new bond formed is likely to influence the choice between the polar and SET routes. The stronger the bond formed, the more steeply the  $D^+A^-$  (polar) curve of Figure 2 drops in energy leading to a corresponding reduction in the activation energy.

The tendency for halogen ions to act as reductants rather than nucleophiles increases in the order  $F^- < Cl^- < Br^- < I^-$ .<sup>12c,d</sup> While this is partly attributed to the oxidation potential of these ions (which manifests itself through the donor-acceptor ability), it is also attributed to the decreasing C-X bond strength along the series. The tendency for sulfur compounds to react as reductants and not just as nucleophiles is also partly attributed to the weakness of the C-S bond (65 kcal/mol).

**Effect of Radical Delocalization.** In order for group coupling between  $D^+$  and  $A^-$  to take place efficiently, the odd electrons on D and on A need to be largely localized on the two atoms which are to bond to one another. Localization of the two spin-coupled electrons thus facilitates a polar pathway. If, on the other hand, the odd electrons are extensively delocalized, such that their position within either or both moieties needs to be described by a number of resonance forms, then coupling will be inhibited and a SET pathway may result.

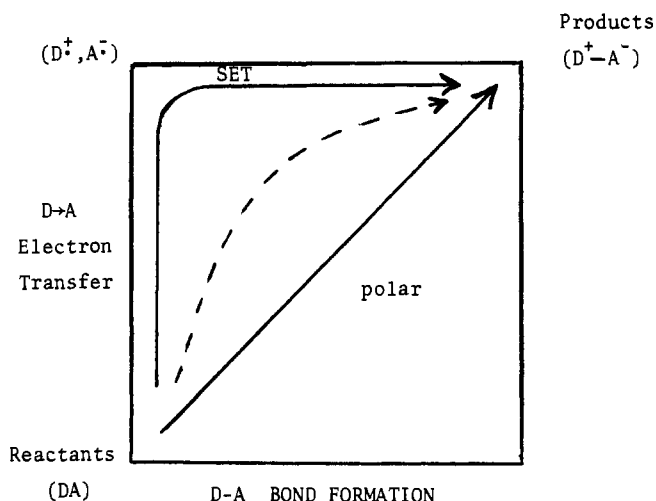
The simplest case of radical delocalization may be demonstrated in the  $S_N2$  reaction.<sup>17b,d,e</sup> On the basis of the two contributors to the three-electron bond of  $(R-X)^-$ , the charge-transfer configuration  $D^+A^-$  may be described by the two VB configurations as shown in eq 7. Note that the odd electron that has been

$$D^+A^- \equiv N \cdot (R-X)^- = a(N \cdot R : X^-) \leftrightarrow b(N \cdot R \cdot X) \quad (7)$$

transferred to R-X is delocalized between R and X groups. When  $R = CH_3$ , then  $a \gg b$  and the odd electron is largely localized on R. Under these circumstances N-R coupling is efficient and the  $S_N2$  pathway is followed. When R is more electronegative however, such as in  $CF_3-Cl$  or  $CCl_4$ , then the electron is likely to be delocalized between R and X ( $a \approx b$ ).<sup>17b,d,e,42</sup> This has the double effect of (a) stabilizing the radical anion  $(R-X)^-$  due to strengthening of the three-electron bond and (b) reducing the likelihood of  $N \cdots R$  coupling. Both factors operate in the same direction, namely, to

(41) For a recent paper on the ability of electrons to transfer over distances of ca. 10 Å see: Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* 1984, 106, 3047.

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**Figure 4.** Potential energy surface diagram illustrating the relationship between polar and SET reaction pathways (indicated by bold arrows). The two axes represent electron transfer ( $D \rightarrow A$ ) and bond formation (between D and A). The possibility of an intermediate mechanism is indicated by the broken line.

favor an electron transfer pathway over the polar  $S_N2$  pathway. Indeed  $CX_4$  molecules are known to react with amines via SET process.<sup>43</sup> The relative kinetic stability of radical cations<sup>44</sup> and anions<sup>30b,45</sup> of polycyclic hydrocarbons is simply understood in these terms since electron transfer to or from a polycyclic hydrocarbon leads to a highly delocalized odd electron.

### Possibility of a Polar-SET Mechanistic Spectrum

Classification is an important part of the scientific methodology. Classifying any observable in terms of one category or another is the first step in ordering the data that has been obtained. An interesting feature of classifications, however, is that invariably one runs into particular cases that seem to not belong unambiguously in one predefined category or another. Classification in terms of black or white invariably leads to the discovery of a gray.

Within the field of mechanistic classification of organic reactions this phenomenon of running into "gray" at some point has been particularly evident. Thus, to quote two well-known examples, the classification of elimination reactions in terms of E1, E2, and  $E1_{cB}$  pathways, and substitution pathways in terms of discrete  $S_N1$  and  $S_N2$  pathways fails to account for all existing experimental data, and a continuous mechanistic spectrum had to be postulated to accommodate such cases. Thus terms such as E2-E1-like and "loose"  $S_N2$  are used to express this "gray" character. The potential energy surfaces models<sup>46</sup> are particularly effective in illustrating this mechanistic continuity.

What is the situation regarding the SET-polar classification? Is a mechanistic spectrum feasible in this

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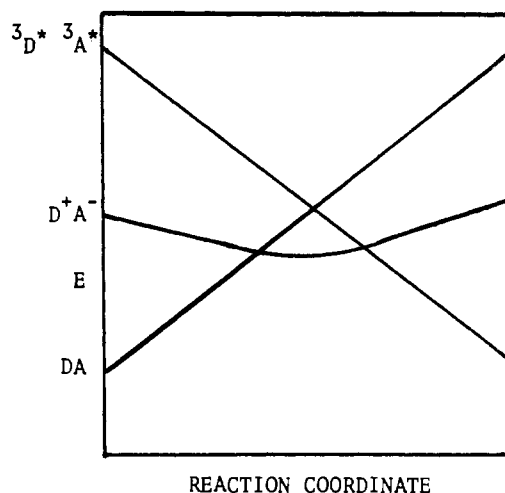
case? The answer appears to be that, here also, a mechanistic spectrum exists. In accordance with our physical representation of a polar process as a synchronous electron and atom transfer, we may describe these two components, as recently proposed by Bethell,<sup>47</sup> using a potential energy surface, (illustrated in Figure 4). In contrast to the normal usage however, only one axis represents a geometric parameter associated with bond formation (D-A bond formation) while the second axis represents an electronic change (electron transfer from D to A).

The relationship between polar and SET pathways now becomes more evident. The SET pathway involves first electron transfer to form  $D^+$  and  $A^-$  species followed by  $D^+A^-$  bond formation and is indicated by the bold curve marked "SET." The polar process, on the other hand, involves synchronous electron shift and bond formation and is indicated by the diagonal arrow marked "polar". In other words, the two mechanisms are distinguished by the degree of concertedness of the electron shift and bond-formation steps. On the basis of Figure 4 it is evident that an intermediate pathway is indeed feasible. This is indicated by the broken line. In this pathway both the electron shift and bond formation are synchronous; however in the early stages the electron shift has moved ahead of the bond formation stage. Indeed Bethell et al.<sup>47</sup> have recently reported the kinetics of hydride transfer between polymethylbenzenes and 9-arylfluorenyl cations and concluded that the reaction proceeds via a transition state characterized by "considerable electron transfer character with loosening of the transferred hydrogen", consistent with the existence of a mechanistic spectrum. Thus there appears to be at least one experimental confirmation of the SET-polar mechanistic spectrum, and we believe that others will be discovered in due course.

### The General Nature of the Electron Shift Process

The fundamental role of the electron shift in organic chemistry may even be discovered in some reactions that do not appear to be electron shift processes. A case in point concerns the class of pericyclic reactions whose reactivity may be understood on the basis of the Woodward-Hoffmann rules.<sup>48</sup> For example, the energy profile for a cycloaddition reaction (e.g., for ethylene and butadiene) may be constructed from the avoided crossing of the reactant DA and the doubly excited product  ${}^3D^*{}^3A^*$  configurations.<sup>17e,18a</sup> In addition, the influence of the singly excited configuration  $D^+A^-$  should also be considered, and a schematic energy diagram of all three configurations is illustrated in Figure 5.

The distinction between "allowed" and "forbidden" cycloadditions may be understood in terms of the allowedness of mixing of the  $D^+A^-$  configuration into the reaction transition state.<sup>17e,18a</sup> If  $D^+A^-$  mixing is symmetry allowed, then the transition state is stabilized and takes on charge-transfer character; an allowed reaction results. If  $D^+A^-$  mixing is precluded by symmetry, then the thermal barrier is too high for the reaction to proceed; the reaction is forbidden. If  $D^+A^-$  mixing is al-



**Figure 5.** Schematic energy diagram that illustrates the major configurations that contribute to any cycloaddition reaction, DA,  $D^+A^-$ , and  ${}^3D^*{}^3A^*$ . For allowed reactions DA and  $D^+A^-$  mix, thereby lowering the activation barrier. For forbidden reactions, mixing of DA and  $D^+A^-$  is precluded by symmetry.

lowed, but the energy of  $D^+A^-$  is high (weak diene and dienophile), the reaction is slow; conversely if  $D^+A^-$  is low in energy (powerful diene and dienophile), the reaction is rapid. Thus, even those reactions governed by the Woodward-Hoffmann rules, which clearly are *not* electron shift or transfer reactions, are also ultimately governed by the energetics of single electron transfer. This interpretation is in agreement with Kochi's recent analyses of the Diels-Alder reaction.<sup>27d</sup> Kochi's observation that the rates of Diels-Alder reactions are also directly related to the energy of the charge-transfer bands of the DA complex formed between diene and dienophile, in analogy with many polar processes, points out most clearly the dominant role of the  $D^+A^-$  configuration in governing the rates of cycloadditions. Other reactions, in which the  $D^+A^-$  configuration serves the role of an "intermediate" configuration, include radical addition to alkenes<sup>49</sup> and carbene insertion.

We see, therefore, that the energetics of the single electron shift appears to dominate much of organic reactivity. Regardless of whether  $D^+A^-$  serves as the product configuration, as it does in most polar processes, or an "intermediate" configuration as it does for radical or pericyclic processes, both the energy and structure of transition states for organic reactions appear to be indelibly stamped by  $D^+A^-$  character.

### Concluding Remarks

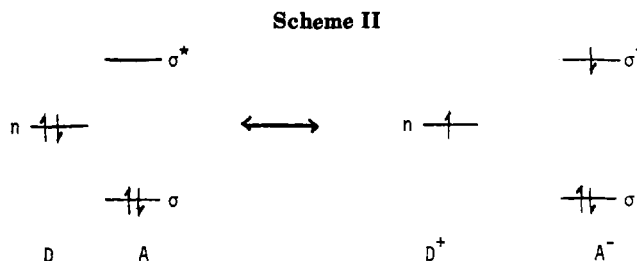
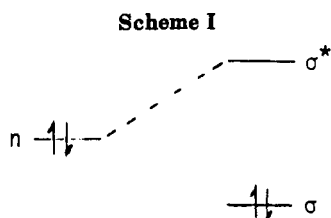
This paper has attempted to demonstrate the central role of electron transfer in organic chemistry. Interestingly, within inorganic chemistry, where a quite different terminology is employed, there is no ambiguity. Single electron transfer is universally recognized as a fundamental process governing inorganic reactivity. In fact on the basis of the inorganic electron transfer terminology,<sup>50</sup> an  $S_N2$  reaction may be considered analogous to an inner-sphere electron transfer! The  $S_N2$  reaction between a nucleophile, N, and a substrate, RX, may be thought of as proceeding via an activated complex in which the reductant (the nucleophile, N) and

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the oxidant (the leaving group, X) are held together by a bridging ligand (R) which is bonded to both. The net result of the reaction is both electron and group transfer. Thus, while the inorganic chemists have chosen to focus on the *electronic* changes, the organic chemists have placed the emphasis on the *atomic* changes that have taken place. However the analogy between the processes is clear.

The notion of the curly arrow, which dominates so much of traditional organic reaction mechanism, is of undoubted utility, and indeed was a mainstay of this author's education in organic chemistry. However, the physical significance of such curly arrows should not be exaggerated. The curly arrow is a most useful mnemonic for describing organic mechanisms but should not be interpreted as a physical description of what actually occurs. Indeed, the curly arrow convention violates one of the fundamental rules of quantum mechanics—the concept that electrons are indistinguishable. The curly arrow description of an  $S_N2$  reaction (eq 1) implies that the two electrons that make up the N–R bond in the product originated from the nucleophile while the R–X bond pair ends up on the leaving group. Conversion of reactants to products appears to be governed by the “movement” of *four* valence electrons. As we have indicated in this paper, a wave function describing reactants

$$2^{-1/2}\{|\phi_N(1)\bar{\phi}_N(2)\phi_R(3)\bar{\phi}_X(4)| - |\phi_N(1)\bar{\phi}_N(2)\bar{\phi}_R(3)\phi_X(4)|\} \quad (8)$$

which may be pictorially represented by the VB form  $N:\bar{R}\cdot X$ , differs from the wave function describing products

$$2^{-1/2}\{|\phi_N(1)\bar{\phi}_R(2)\phi_X(3)\bar{\phi}_X(4)| - |\bar{\phi}_N(1)\phi_R(2)\phi_X(3)\bar{\phi}_X(4)|\} \quad (9)$$

pictorially represented by the VB form  $N\cdot R :X^-$  by just

a single electron shift—from N to X ( $\phi_N$ ,  $\phi_R$ , and  $\phi_X$  represent hybrid orbitals on N, R, and X, respectively). The act of shifting the single electron from N to X may occur either with or without free radical formation. Normally, the concerted process is energetically favored. However formation of radicals may occur when group coupling is inhibited by steric or electronic effects.

Oddly enough, frontier molecular orbital (FMO)<sup>51</sup> theory may have contributed to the misconception that somehow two electrons are involved in polar processes. The  $S_N2$  reaction is commonly treated in FMO theory by the interaction between a doubly occupied nucleophile orbital, n, interacting with a vacant  $\sigma^*$  orbital, as indicated in Scheme I. It appears as if two electrons are involved. However, this mixing process transfers only slight electronic charge from  $n \rightarrow \sigma^*$ . Indeed, a description of MO orbital mixing in terms of MO configurations again merely leads us to a  $DA-D^+A^-$  mixing (Scheme II) and a single electron shift.

Finally, we opened this paper with the statement that chemical reactions take place as a result of the rearrangement of valence electrons. What could be intellectually more satisfying than the profound realization that the simplest possible electronic reorganization—the shift of one single electron—is the fundamental act that governs so much of chemical reactivity. We believe this realization opens many doors in the quest for greater chemical understanding.

*Helpful discussions with James Becker, Don Bethell, Nathan Lewis, and Sason Shaik as well as critical comments by Larry Miller are gratefully acknowledged. The author is especially indebted to John Brauman for his gracious hospitality during a sabbatical leave at Stanford University where this manuscript was concluded.*

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